

DRD NO. SE-7
DRL NO. 60

DOE/JPL 954888 79/3
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CONTINUOUS CZOCHRALSKI GROWTH

SILICON SHEET GROWTH DEVELOPMENT
OF THE LARGE AREA SILICON SHEET TASK
OF THE LOW COST SILICON SOLAR ARRAY PROJECT

SEVENTH QUARTERLY PROGRESS REPORT
APRIL 1 - JUNE 30, 1979
PROGRAM MANAGER: R. L. LANE
PRINCIPAL INVESTIGATOR: E. ROBERTS

KAYEX CORPORATION
1000 MILLSTEAD WAY
ROCHESTER, NEW YORK 14624

"The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DoE."

(NASA-CR-162589) CONTINUOUS CZOCHRALSKI
GROWTH. / SILICON SHEET GROWTH DEVELOPMENT OF
THE LARGE AREA SILICON SHEET TASK OF THE LOW
COST SILICON SOLAR ARRAY PROJECT Quarterly
Progress Report, 1 Apr. - 30 Jun. 1979
N80-70381
Unclas 46100
00/44



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ABSTRACT

During this reporting period, a major effort was put into improving the yield of high quality silicon crystals grown during continuous runs. It was felt that this objective could be accomplished by eliminating any possible areas of furnace or melt contamination. The areas of possible contamination are listed in this report in Section 2.2.1.

Mechanical checks and calibrations were stressed to make sure the machine was acceptable by production specifications. A preventative maintenance program was also initiated to make sure that the machine remains in good condition for growing crystals. As a result of these efforts, we were able to improve our yield of high quality crystal as evidenced by Runs No. 41 (66%) and No. 47 (88%). It was disappointing that neither of these continuous runs resulted in 100 kg or more pulled. However, we feel that our efforts this quarter have been in the right direction. Moreover, if it had not been for a crucible failure, we feel that Run No. 47 could have continued to the 100 kg goal.

Samples from Run No. 30 were tested for impurity concentrations with results which indicate that contaminants may have been present. These results indicate that more work and study is needed in the areas of melt contamination and furnace atmosphere analysis.

Hot melt replenishment methods and capabilities for lump recharging were developed to the point where it is now possible to dump 15 kg of lump silicon into a 12" crucible in one recharge cycle using a two step method.

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1.0 INTRODUCTION

The purpose of this program is to demonstrate the growth of at least 100 kilograms of single crystal ingot from one crucible by the Czochralski (CZ) method.

The approach to the continuous growth process being pursued in this effort relies on conventional CZ technology combined with new equipment designs which allow repeated alternate cycles of crystal growth and hot melt replenishment by methods which are suitable for use in a high volume production facility.

A Hamco Model CG2000 crystal grower was modified with a special chamber for the storage of a supply of polycrystalline silicon and a vacuum-tight isolation valve to permit retrieval of crystals and melt replenishment without contamination. A number of additional modifications to the facility have been completed in the program, and the process study phase is now under way, with a number of multi-ingot runs having been performed.

It is the purpose of this contract extension to describe a program aimed at a more accurate cost analysis of the continuous growth of silicon into material and also an investigative program for the purpose of defining and solving problems which may hinder the development of continuous Czochralski growth.

The proposed work consists of two efforts, the first being to conduct a series of continuous crystal growth runs in a pilot-plant-type operation. This is for the purpose of establishing with more certainty the costs of the process and pushing the technology even farther from the present laboratory operation toward production. The second (and parallel) effort will be to conduct an investigation study in the areas which appear to be related to yield of high quality crystal, specifically the quality of the crucible, the effect of impurities on degradation of the crucible, the introduction of impurities into the silicon, and the effect of the furnace hot zone parts on the process, specifically in terms of impurities or foreign particles

introduced into the silicon from its environment.

2.0 PROGRESS

2.1 Hot Melt Replenishment

As stated in the Twentieth Monthly Progress Report, May 1 - 31, 1979⁽¹⁾, we are continuing to develop the maximum capabilities of the lump recharging method. In June, during Run No. 47, we were able to improve upon the ability to recharge more than 10 kg of lump silicon per recharge cycle. During one recharge cycle in Run No. 47, the hopper was filled with 15 kg of lump silicon. It is not possible to dump all 15 kg at once into a 12" crucible with a normal amount of residual melt. Therefore, a two step dumping procedure was attempted with satisfactory results. The first step was to lower the hopper and dump the silicon lumps according to the normal procedure. By monitoring the weight, we were able to stop dumping the lumps after a certain weight of silicon had been dumped by raising the hopper and closing the opening. After the silicon dumped during the first step was nearly melted, we again lowered the hopper and dumped the remainder of the silicon. During this recharge cycle, 7.8 kg was dumped during step one and 7.2 kg was dumped during step two. The total melt size after this recharge cycle amounted to 23.5 kg in a 12" crucible. The results were successful. This new procedure allows us to recharge up to 15 kg without opening the pull chamber door and reloading the hopper.

2.2 Crystal Growth Development

2.2.1 During this quarter, our top priority was to improve the yield of high quality crystal grown during continuous runs and single runs. We felt that this could best be accomplished first by elimination any possible areas of furnace or melt contamination. We considered the following areas:

1. Air Leaks
2. Water Leaks

3. Raw Material (silicon)
4. Etching Procedure
5. Carbon Parts
6. Volatile Matter (grease, etc.)

Extensive leak checking was performed during this reporting period to identify and eliminate any possible air leaks in the furnace system. A preventative maintenance program was initiated during this period. Also, an attempt is being made to determine the reliability of instruments used to measure vacuum in the furnace system. By the end of the quarter, we felt we had an air tight machine.

As previously reported, a water leak was discovered in a failed weld during this quarter. A new top plate was fitted, eliminating this source of contamination. However, it is not possible to detect an interior water leak in the furnace system by leak testing or vacuum readings. The leak was found by visual observation.

There has been little work done on identifying possible contaminants from virgin silicon or recycled silicon. To date, only a few samples have been sent out for impurity analysis. We more or less have to rely on our vendors to provide us with high quality raw materials.

Our etching facilities are not as good as we would like. We have improved our procedures for etching, rinsing, drying and handling the silicon. Very little investigation has been done to determine the purity of the silicon prepared in this way. However, this is not relevant to virgin polysilicon used for continuous runs. Our objective is to arrive at an acceptable procedure for the equipment that we have and then attempt to make it as reproducible as possible.

Possible contamination from carbon parts has been a constant concern throughout this contract and the previous contract. It has been demonstrated in the past that a melt down attempted under hard vacuum (no argon flow for cleansing the melt surface) can result in a high carbon content scum to be formed on the melt surface. We feel that it is essential that the carbon parts in the furnace be of high quality. It must be free of volatile materials and be dense enough to eliminate outgassing that would force carbon particles into the furnace atmosphere where they might be blown into the crucible and come into contact with the melt. Another possible detrimental effect of poor quality carbon is possible devitrification of the crucible wherever it comes into contact with the carbon parts (upper and lower supports).

Satisfactory bakeouts are always necessary for carbon parts, especially new ones. However, these bakeouts may still not eliminate problems caused by poor quality carbon parts. Again, we must rely on our vendors to provide us with high quality carbon parts.

Part of this contract extension provides for runs performed with halogen purified graphite parts.

Other information concerning carbon contamination of silicon can be found in "An Unsolicited Proposal for Continuation of JPL Project 954888", January 22, 1979⁽²⁾.

An area of possible contamination that we felt we had significant control of was the area of volatile matter being introduced into the furnace atmosphere from a source not directly related to or needed to grow crystals, for example, vacuum grease on O rings and other types of seals used to make the furnace air tight. The types of materials being used were investigated and found to be detrimental to the crystal growth process. A silicone base

vacuum grease was substituted for the vacuum grease being used. However, it has been learned now that silicone vacuum grease will oxidize at temperatures above 450°F. Silicon dioxide powder results from oxidation along with highly volatile methyl groups.

We spent a considerable amount of time this quarter identifying areas of volatile matter contamination, removing the possible contaminants and making sure that the area was still air tight. By the time Run No. 47 was attempted, we felt confident that this area of possible contamination had been eliminated.

2.2.2 We have started to look at the relationship between argon and silicon monoxide flow patterns in the furnace. Of interest is what causes monoxide to be deposited on the crystal as it is being grown: is this monoxide detrimental to crystal growth and can the flow patterns in the furnace be altered to eliminate this monoxide coating without adversely affecting the thermal condition of the furnace? Areas to be considered are:

1. Amount of argon flow - furnace vacuum and valve settings.
2. The height of the crystal at which the monoxide starts to deposit.
3. The effects of the crucible starting position in relation to the heater.
4. Exhaust mechanisms and methods.

To date, we feel that monoxide on the grown crystal is not a cause of structure loss unless the monoxide is contaminated by other substances which could cause loss of structure.

2.3 60 Kilogram Run No. 47

Tables 1 and 2 summarize the results of the 60 kilogram (Run No. 47). Tables 1 and 2 are a standard for reporting a continuous run in the past. Crystal size was similar to Run No. 30. However, the average growth rate was lower. It was felt that conservative pull speeds would increase the yield of

SUMMARY OF RUN NO. 47

CRYSTAL INGOT DIAMETER	12.7 cm to 13.5 cm
AVERAGE GROWTH RATE	6.8 cm/hr
RUN TIME	51.6 hrs
THROUGHPUT	1.17 kg/hr
PULLED YIELD	92.5%
HIGH QUALITY CRYSTAL	88.3%
TOTAL INGOT PULLED	60.2 kg

TABLE 1

RE CHARGE AND INGOT GROWTH TIME (RUN 47)

MELT NO.	RECHARGE TIME (HR) (1)	COMMENTS	CRYSTAL GROWTH TIME (HR) (3)
1	2.5 (2)	5.0 kg Lump Hot Filled	3.5
2	1.8	10.0 kg Lump	7.0
3	2.0	15.0 kg Lump by Two Step Method	10.2
4	2.5	10.0 kg Lump, Cycle 1 8.0 kg Lump, Cycle 2	.8 then melt back 2.0
5	No Recharge		<u>7.4</u>
Total	8.8 Hr		30.9 Hr

- (1) Recharge Time includes: Removal of grown crystal
Insertion of hopper
Dump hopper charge
Melt down
Seed preparation up to seeding the melt
- (2) Includes cold fill and hot fill time on first melt.
- (3) At growth diameter 127 mm to 135 mm.

NOTE: Total Run Time = 51.6 hours. 11.9 hours were devoted to neck, crown growth, and melt backs.

TABLE 2

high quality crystal until thermal gradient parameters could be optimized in the furnace. Even with the slower growth rate, the overall throughput was nearly the same as Run No. 30. This was possible due to the decreased time used in recharging procedures.

The percentage of time devoted to actual crystal growth at full diameter was higher on this run, 60% as opposed to 50% during Run No. 30. The amount of run time used for recharging was lowered from 25% in Run No. 30 to 17% in Run No. 47. The remainder of the run time was used for neck growth, crown growth, and melt backs of crowns or crystals that may have lost structure early into the run.

The yield of high quality material improved dramatically with this Run (88.3%). It was felt that if the crucible had not failed due to excessive devitrification, the run may have continued to the 100 kg goal with good results.

It is not known why the crucible failed, but there is the possibility that new carbon parts installed prior to this run were either of poor quality or insufficiently baked out. The possibility of an inferior crucible also exists. A sample of the crucible will be sent out for analysis.

A decision was made after the 5th crystal had been grown to terminate the run at this point due to the dangerous condition of the crucible (large inward bulges).

While we were preparing to take a sample of the residual melt, we noticed small visible pieces of quartz floating on the melt.

2.4 Sample Preparation and Analysis

After Run No. 47, it was decided in a meeting with the project monitor not to send out a full complement of samples for testing. It was agreed to send out a small set of representative samples instead.

Results of solar cell analysis and impurity analysis on Run No. 30 have

been reported in earlier reports. Based upon these results, it is felt that more study is needed in the area of impurity analysis of silicon samples and also impurity concentrations in the furnace atmosphere. Based on our information to date, we feel that high quality crystals may be advantageous to obtaining high efficiency solar cells desired.

3.0 CONCLUSIONS AND DISCUSSION

The objective of improving the yield of high quality silicon crystals has been achieved - Run No. 41 (66%) and Run No. 47 (88%). We believe this is a direct result of identifying the possible areas of furnace atmosphere contamination and melt contamination and concentrating on eliminating as many sources of contamination as possible. Even though these two runs did not last for the entire 100 kg goal, we feel that, barring a mechanical failure, the 100 kg goal can be achieved with acceptable yields of high quality silicon crystal. The throughput on these two runs was very close to the throughput projected for crystals grown from 12" crucibles - 1.2 kg/hr.

We have experienced a certain amount of success with the lump recharging device which has enabled us to exceed our initial estimates of the capabilities of the hopper and lump method of recharging. We have been able to decrease the amount of run time devoted to recharging (refer to Section 2.3) from 25% to 17%.

Possible sources of melt contamination and furnace atmosphere contamination have been identified. Efforts have been made and are continuing to eliminate all possible sources. Since certain types of data are necessary to determine if improvements have actually occurred, we feel it is essential to send representative samples out for impurity analysis. This is being done and will continue in the future.

4.0 PLANS

The decision has now been made by all persons directly responsible for the

project to convert the JPL furnace hot zone to 14" parts. We will not go back to 12" parts unless it is determined that it is not possible to achieve the project's goals by using the 14" parts.

Process parameters will be evaluated for the 14" set up and changed as necessary to improve the system to meet our objectives. Mechanical parameters will also be evaluated and corrected where necessary - for example, effects of more weight per crystal.

Further study and work will be performed to not only eliminate possible sources from contamination, but also to prevent these sources from recurring.

More samples will be sent out for impurity analysis so that we can attempt to define the relationships between contaminant concentrations and structure loss mechanisms.

REFERENCES

- (1) R. L. Lane, "Continuous Czochralski Growth", Twentieth Monthly Progress Report, DOE/JPL 954888, May 1 - 31, 1979.
- (2) R. L. Lane, "An Unsolicited Proposal for Continuation of JPL Project 954888", January 22, 1979.

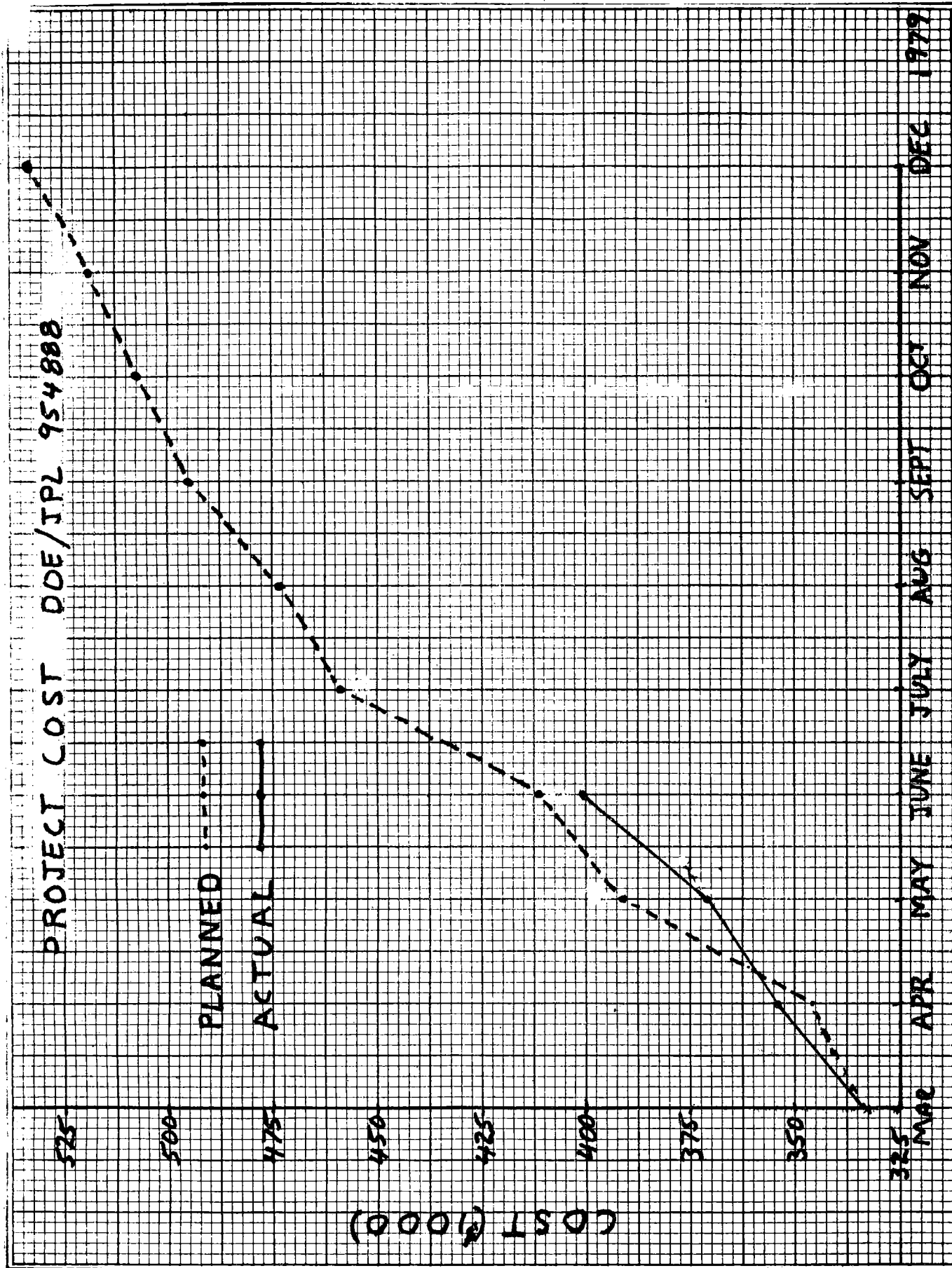
PROGRAM PLAN - CONTINUOUS CZ DEVELOPMENT

PROJECT GOALS	1979					OCT.	NOV.	DEC.
	APRIL	MAY	JUNE	JULY	AUG.			
A. 100 KG CONTINUOUS RUNS								
1. SCHEDULE OF RUNS	●	■	▼	▼	▼	▼	▼	▼
2. SAMPLE PREPARATION & ANALYSIS (ALL RUNS)		●	■					
3. SOLAR CELL ANALYSIS (ALL RUNS)			○	○	▼			
4. ECONOMIC MODEL, UPDATE	●	■		▼	▼			▼
B. PROCESS DEVELOPMENT RUNS (10 TOTAL)								
1. RUN SCHEDULE	●	▼	▼	▼	▼	▼	▼	▼
2. CRUCIBLE COMPARISON, ANALYSIS	●	■		▼				
3. GRAPHITE PURIFICATION, ANALYSIS		●	■					
4. HIGH PURITY RUNS					○	▼		
C. REPORTS		●	■	▼	▼	▼	▼	▼

5.0 COSTS AND MAN HOURS

	<u>PRIOR REPORTED</u>	<u>CURRENT MONTH</u>	<u>TOTAL</u>
Man Hours	10,452.0	614.5	11,066.5
Costs	\$ 371,695	\$ 31,336	\$ 403,031

Not included in these figures is a total of 108 hours of overtime worked. This would yield a total man hours' figure of 11,174.5 hours.



DIRECT LABOR HOURS DOE/JPL 954880

PLANNED
ACTUAL

1000 HOURS

MAR APR MAY JUNE JULY AUG SEPT OCT NOV DEC 1979

